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Chemical Imaging of Phase-Separated Polymer Blends by Fluorescence Microscopy

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Blends of poly(vinylacetate) (PVAc) and poly(cyclohexylmethacrylate) (PCHMA) labeled by copolymerization with 4-methacryloylamine-4'-nitrostilbene (Sb), with (1-pyrenylmethyl)methacrylate (Py), or with 3-(methacryloylamine)propyl-*N*-carbazole (Cbz) were prepared by casting dilute solutions in tetrahydrofuran (THF) or chloroform. Films about 10 μm thick were formed. Phase separation in two types of domains is observed by transmission optical microscopy (TOM) and epifluorescence microscopy (EFM): small craters of 1 to 10 μm placed at the polymer-air interface and larger domains, on the scale of 100 μm . The morphology of samples depends on the composition of the polymer blend and on solvent. The green fluorescence of Sb, the violet of Py, or the blue of Cbz provides imaging of the distribution of PCHMA in the different domains and in the matrix. It is thus observed that (i) superficial craters and large domains are formed mainly by PCHMA and (ii) the matrix is composed of PVAc in films cast from THF and it is a blend of the two polymers, homogeneous at the submicrometric scale, for chloroform. The emission intensity of Py, recorded by microfluorescence spectroscopy (MFS), yields a mapping similar to imaging detection. It is remarkable that in films cast from chloroform, the smaller domains are distributed with a 2D hexatic order disrupted by dislocations and disclinations, whereas in films cast from THF, a larger heterogeneity is found, denoting different mechanisms of solvent evaporation.

KEY WORDS: Fluorescence microscopy; chemical imaging; polymer blends.

INTRODUCTION

Polymer blends [1] are the base of particularly interesting materials. When they are single phase, they normally show properties in between those of the monocomponent systems, as in the case of Noryl, which is based on a compatible blend of polystyrene and poly-*p*-phenyleneoxide. Multiphasic blends may show new or improved properties, as for high-impact polystyrene, an incompatible blend of polystyrene and polybutadiene.

The criteria of polymer compatibility depend on the scale at which a measured property is sensitive. For example, it was demonstrated [2] that fluorescence techniques

are sensitive to lower-scale phase separation than standard techniques such as differential scanning calorimetry (DSC). Optical microscopy [3] has the advantage of visualizing phase separation on the scale of micrometers, but it has some limitations related to the refractive index of the phases and, besides, it may not distinguish between physical defects and changes in sample composition. It seems thus reasonable to combine microscopy and fluorescence techniques.

Epifluorescence microscopy (EFM) and microfluorescence spectroscopy (MFS) were successfully employed to characterize phase-separated polymer blends [4–7]. Some other more sophisticated microscopic fluorescence techniques [8–10] were also applied to analyze the morphology of heterogeneous films.

In this work, both EFM and MFS are employed to study the morphology of films prepared by casting dilute

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solutions of poly(vinylacetate) (PVAc) and poly(cyclohexylmethacrylate) (PCHMA). Acrylic polymers, alone or blended with vinylics, are broadly employed in solvent-borne coatings. The defects of film coatings and their optical properties are strongly related to solvent evaporation mechanism. Here we analyze solvent effects on the morphology of films formed by PCHMA/PVAc blends.

EXPERIMENTAL

4-Methacryloylamine-4'-nitrostilbene (Sb) and 3-(methacryloylamine)propyl-*N*-carbazole (Cbz) were synthesized as reported previously [11,12]. (1-Pyrenylmethyl)methacrylate (Py) was purchased from Polysciences and used as received. Poly(cyclohexylmethacrylate) (PCHMA) samples labeled with Sb, Py, or Cbz were obtained by radical copolymerization of cyclohexylmethacrylate and the corresponding methacrylate bearing the desired chromophore. In the polymerization feeding mixture, the total comonomer concentration in dioxane solutions was 23% (w/w), with 1% (w/w) labeled comonomer and 1% (w/w) AIBN as initiator. Polymerizations proceeded at 60°C, and afterward, polymer samples were dissolved in THF, precipitated on methanol, and dried under vacuum at room temperature, overnight.

The chromophore molar fraction in the copolymers (F_c) was determined by spectrophotometry (Perkin Elmer Lambda 4). Intrinsic viscosities of labeled PCHMA in THF were measured at 30°C in an automatic Schot Viscometer, and the corresponding molecular weights were calculated with the viscosimetric equation of the homopolymer, taken from Ref. 13. Measurements of the glass transition temperatures (T_g) were performed in a Perkin Elmer DSC-7. Only third-run transitions were taken into account.

PVAc, with a molecular weight of 9×10^4 , was purchased from Polysciences and used without any further purification. Table I summarizes the characteristics of the samples employed in this work.

Table I. Characteristics of the Samples: Viscosity-Average Molecular Weight (M_v), Glass Transition Temperature (T_g), and Molar Fraction of Chromophore in Labeled PCHMA Samples (F_c)

	$M_v \times 10^{-3}$	T_g (°C)	F_c (% mol)
PVAc	90	41	—
PCHMA(Py)	116	82	0.20
PCHMA(Sb)	81	72	0.49
PCHMA(Cbz)	78	74	0.20

Solutions of PVAc and labeled PCHMA in THF or Cl_3CH , with 2% (w/w) total polymer concentrations and different weight fractions of each polymer, were cast on coverglass plates at room temperature. Glass plates were previously silanized with methyltrichlorosilane. Two casting procedures were employed, in open air (quick evaporation) and in a closed vessel with an atmosphere saturated with the solvent (slow evaporation). The resulting films were circular, with diameters of about 1 cm, and 10 μm thick. The border of the film, a crown of about 2 mm, was excluded from observations.

Two microscopes were employed. (i) A Nikon Labophot (provided with photographic and CCD cameras plus videoprinter from SONY) was employed for transmission optical microscopy (TOM) and epifluorescence microscopy (EFM) imaging observations. Objectives of $\times 10$, $\times 40$, and $\times 100$ with NA of 0.25, 0.65, and 1.25, respectively, were used. In EFM measurements, a 100-W Hg arc lamp was employed for excitation. It was filtered to transmit in the range 330–380 nm for Py and Cbz and 450–490 nm for Sb. The emission was separated from the excitation beam by a dichroic mirror ($\lambda_{\text{ex}} < 400$ nm for Py and Cbz, $\lambda_{\text{ex}} < 510$ nm for Sb) and a barrier filter ($\lambda_{\text{em}} < 420$ nm for Py and Cbz, $\lambda_{\text{em}} < 520$ nm for Sb). (ii) Microfluorescence-spectroscopy (MFS) measurements were performed with an inverted microscope Axi-overt 100 TV (Carl Zeiss Jena) coupled with a 400- μm optical fiber to an Acton Spectro-Pro-150 monochromator. More details are given in Ref. 4.

RESULTS AND DISCUSSION

Polymer Compatibility

The first question concerning polymer blends is whether or not they are compatible on a given scale determined by the employed technique. Films prepared by casting dilute solutions of PCHMA and PVAc may be turbid or transparent, depending on the solvent used (THF or Cl_3CH), the sample composition, and the PCHMA characteristics (e.g., molecular weight, polydispersity, side chains). When prepared with PCHMA samples, whose characteristics are summarized in Table I, films with compositions of 20/80, 50/50, and 80/20 were turbid. Nevertheless, films with only one component (PCHMA) cast from THF are turbid, whereas those cast from chloroform are transparent. These results render the compatibility of PCHMA and PVAc uncertain and discard turbidity as a criterion of polymer incompatibility.

TOM images (Fig. 1a) of films cast from THF solutions show a heterogeneous aspect. Films with com-

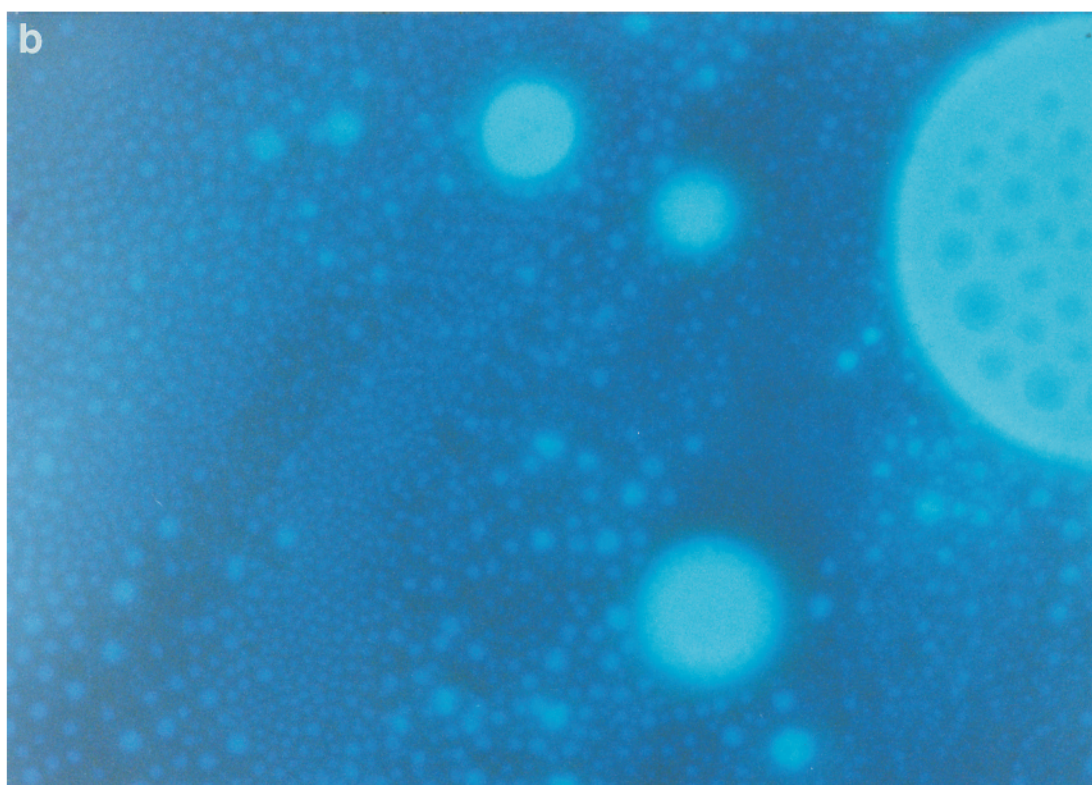
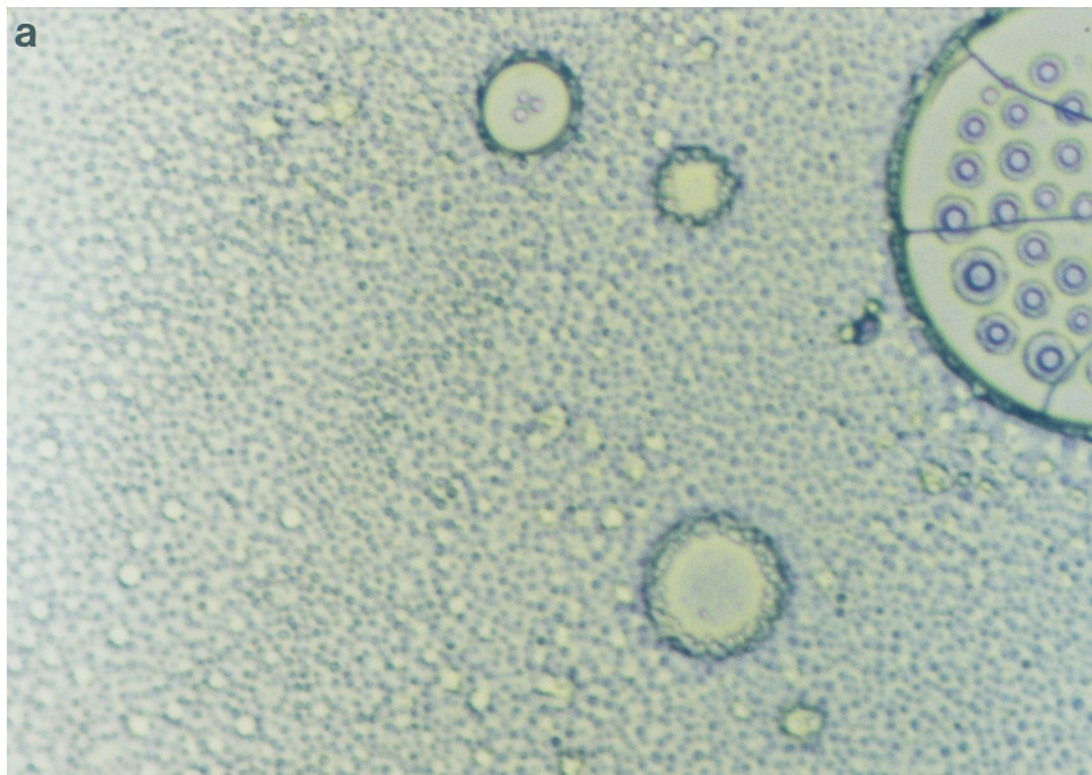


Fig. 1. TOM (a) and EFM (b) images of the 20/80 PCHMA(Py)/PVAc blend cast from dilute THF solution. The scale bar corresponds to 100 nm.

positions 20/80 and 50/50 show droplet-in-matrix morphologies containing domains in two size scales: large domains, in the range of 100 μm ; and much smaller domains, of about 1 μm . The small domains are on the air–polymer interface (since they are the only type of domains observed by SEM [13]) and they are crater-like voids, as observed by TOM using an additional lateral illumination. Films with compositions of 80/20 show a more complex interconnected morphology.

Films prepared by casting from Cl_3CH are much more homogeneous, in particular, the 20/80 compositions of the three PCHMA samples and the 80/20 composition prepared with PCHMA(Py), the highest molecular weight PCHMA sample. But the small domains are still observed in 20/80 films, increasing the magnification to 100 \times .

Fluorescence Imaging

Fluorescence imaging is thus quite useful to identify these two types of domains as well as the matrix composition. Films containing 20% (w/w) PCHMA cast from THF solutions, observed with EFM (Fig. 1b), show large and small domains: blue for Cbz, violet in the case of Py, and green in the case of Sb. The darkness surrounding those fluorescent spherical domains means that the matrix is pure PVAc, which of course is nonemitting, whereas the domains seem to be pure PCHMA or a PCHMA-rich blend with PVAc.

The matrix is slightly colored in the case of films cast from Cl_3CH , indicating that it is constituted by a blend of the two polymers. Table II shows the average emission intensity of Py in different regions of blends measured at a constant wavelength (393 nm) by MFS. Assuming that the maximum intensity for each solvent corresponds to domains of pure PCHMA(Py), the composition of the matrix and of the domains with lower emission intensity can be estimated (Table II). It is thus confirmed that some degree of compatibility exists in blends prepared with Cl_3CH and that matrix compositions are very much solvent dependent.

Table II. Fluorescence Intensity of PCHMA(Py) (λ_{ex} = 335 nm, λ_{em} = 393 nm) in Different Parts of PCHMA(Py)–PVAc Blends Cast from Chloroform or from THF Solutions: Numbers in Parentheses Are the Fractions of PCHMA(Py) in that Region

Global	Matrix		Domains	
	THF	Cl_3CH	THF	Cl_3CH
(20%)	50 (5%)	220 (20%)	600 (80%)	—(0%)
(50%)	0 (0%)	500 (40%)	750 (100%)	1300 (100%)
(80%)	50 (5%)	500 (40%)	650 (90%)	800 (60%)

That is the most relevant solvent effect, but small differences in the distribution of the small domains can also be observed in films cast from THF or from Cl_3CH solutions.

Origin of the Small Domains

In some films of blends cast from Cl_3CH it was found that the small surface craters were distributed in a 2D hexatic order, as shown by Voronoi tessellation. The centers of craters were located about equally separated along sets of curved parallel lines frequently disrupted by defects.

Even more, in films of pure PCHMA cast from Cl_3CH , there were also very small domains which seem to be aligned in straight lines, forming a network pattern very similar to the shear banding patterns formed in plastically deformed tough polymers.

Films cast from THF, for both blends and a single component (PCHMA), did not show the small craters but also large empty holes, which suggests [10] that bubbles were formed during THF evaporation. As a consequence of the formation of holes, the macroscopic aspect of films was heterogeneous and turbid.

The existence of defects such as holes or craters, and its chemical composition in the case of blends, indicates a different mechanism of film drying which will be analyzed in the light of solvent properties [14].

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